

## MULTILAYER COMPOSITE FILM AND USE OF THIS FILM

9/2  
5 The present invention relates to a multilayer composite film of food grade quality, the thickness of which is between 30  $\mu\text{m}$  and 120  $\mu\text{m}$ , comprising a layer based on PP sandwiched between two outside layers of LLDPE, the density  $d$  of which is between  $0.919 < d < 0.930 \text{ g/cm}^3$ , and to a use of this film.

9/3  
10 Multilayer composite films are well known and are generally intended to combine the physical or chemical properties of various polymer materials according to the desired properties.

09875484 060601  
15 EP 0 247 896 discloses a weldable film comprising a base layer which contains a polyolefin, which on at least one of its sides has 1 to 20% by weight based on the base layer of a film containing a blend of 70 to 95% by weight of an ~~LLDPE~~ and 5 to 30% by weight of a resin with a molecular weight lower than that of the LLDPE.

20 Another weldable multilayer film based on polypropylene comprising at least one outside layer of LLDPE of which the density is from  $0.893\text{--}0.905 \text{ g/cm}^3$ , the melt index from 0.1-10 g/10 minutes and containing up to 20% of a comonomer, in JP 09 207294. [sic]

25 JP 09 314769 describes a weldable film comprising a film of flexible resin of the polypropylene type onto the opposite faces of which LLDPE films are laminated.

30 JP 10 272747 relates to a stretchable film with three layers or more comprising, at its surface, a layer of LLDPE and a layer of amorphous copolymer and, by way of middle layer, a blend of polypropylene (C), of poly(1-butene) (D) in a ratio  $(C)/(D) = 0.10\text{--}9.0$ . A surfactant of nonionic type is combined with one or  
35 more of the layers.

US 5 085 927 proposes to increase the molding property of a stretchable film by adding an elastomer

compound in addition to the adhesion promoters which in themselves increase the molding properties of the film.

Elsewhere, particularly in WO 98/28199, there has been proposed a sachet for packaging liquid, comprising a valve for controlling the dispensing of the liquid, consisting of the superposition of two films welded along two non-converging lines to form a dispensing passage by the parting of these two films. This passage preferably has an entry passageway, the perimeter of which corresponds to that of a straw, the end of which is bulged. This film has enough elasticity to allow it to expand as this straw is being introduced and to then close up around it to prevent it from being withdrawn from said passage. The straw is thus secured to the sachet and can only be withdrawn by the amount necessary to allow the passage forming the valve to close.

The material of the film forming the valve has therefore to have enough elasticity to close up around the straw while at the same time allowing the bulged part to pass. This film has to be compatible with drinks and therefore meet standards relating to food products. As a preference, this material has to maintain its properties even after it has been subjected to a temperature of between 80° and 90°C, which is frequently that of the drink at the time that it is packaged in the sachet.

The combination of all these properties, some of which are contradictory, is not easy to achieve even with combinations of several layers of different polymers. In particular, none of the abovementioned documents of the prior art allows these properties to be combined.

It is an object of the present invention to obtain a film capable of meeting at least the main requirements, that is to say, in addition to the properties of flexibility needed to allow the passage that forms the valve to close in a sealed manner, the properties of elasticity and of compatibility with food

09875482 060601

2002  
2002

standards. As a preference, the film according to the invention should withstand the temperature of the liquid to be packaged, which may be as high as 80° or even 90°, while keeping its flexibility and elasticity properties intact.

To this end, a very first subject of the invention is a multilayer composite film of the abovementioned type ~~as defined by claim 1.~~ Another subject is a use of this film, <sup>and various</sup> ~~as defined by claim 7.~~

10 ~~Various preferred embodiments of the composite film correspond to the definitions given in the claims dependent on claim 1.~~

Tests carried out with the multilayer film that is the subject of the present invention have shown that such a film makes it possible to meet all the abovementioned requirements, both as regards the valve and as regards the ability to hold the straw in the valve passage and obviously to introduce this straw into this passage. This film also allows all these properties to be maintained after the liquid has been packaged at a temperature of at least 80°C and which may be as high as 90°C.

The invention will be better understood upon reading the examples which follow.

According to one embodiment, the two outside layers of the multilayer film that is the subject of the present invention are made of an LLDPE (Linear Low Density Polyethylene), Dow Elite® 5110, the density d of which is 0.925 g/cm<sup>3</sup> and the melt index MI of which is 0.85 g/10 minutes according to the ASTM D 1238 standard, measurements taken at 230°C, applying a mass of 2.16 kg, with a standard nozzle 2.095 mm in diameter, with the Vicat softening temperature T<sub>v</sub> being 113°C. As a preference, a slip agent, in this example 900 ppm of Erucamide® which is a derivative of erucic acid, the molecule of which is cis-13-docosenamide, is added to at least one of the two outside layers of the film, that is to say to the one which will be on the inside of the passage forming the valve and which will

09675482 060601

therefore be in contact with the straw for withdrawing the liquid so as to make it easier to slide inside the passage forming the valve produced using the film that is the subject of the present invention.

5           The middle layer of this film sandwiched between the abovementioned outside layers consists of a blend of 60% of PP, Moplen® EP-Q 30RF by Himont, a heterophasic copolymer the density  $d$  of which is 0.9 g/m<sup>3</sup>, the melt index MI of which is 0.8 g/10 minutes  
10 according to ASTM D 1238/L and the Vicat softening temperature  $T_v$  of which is 150°C. This middle layer also contains 20% of the LLDPE used to form the two abovementioned outside layers and 20% of a thermoplastic polyolefin, Adflex® Q100F manufactured by  
15 Himont, the density  $d$  of which is 0.89 g/cm<sup>3</sup> and the melt index MI of which is 0.6 g/10 minutes according to ASTM D 1238.

          The role of this thermoplastic polyolefin is to provide the polypropylene with enough elasticity to  
20 allow the film forming the valve and, in particular, the entry passage opening into the actual valve proper, to deform elastically when a bulged retaining part of the straw for withdrawing the liquid passes as it is introduced into this valve. What happens is that the  
25 length of the perimeter of this entry passage is chosen to correspond to that of the perimeter of this straw, so that once the bulged retaining part of this straw has been introduced, the passage closes up around the straw and prevents it from coming back out.

30           This middle layer of the film that is the subject of this invention also has the role of giving this film resistance to a temperature of 80° or to 90°C, so as to allow the enclosures or sachets, to which the valve formed by the film that is the subject  
35 of the present invention is attached, to be filled with drinks packaged at such temperatures. This hot-filling is performed for all sorts of drinks, particularly milk or milk-based drinks, and fruit juices. It must

09875432-060601  
T09090-2845/860

maintain its properties, particularly its elastic properties, after the drink has been hot-packaged.

The film thus manufactured has also to be able to be welded without the welding causing it to degrade, that is to say that the film has to maintain its food compatibility with the drinks packaged.

The various tests carried out to develop this multilayer film have made it possible to observe that while the thickness of the film can be varied in a fairly broad range depending on the requirement, from 30  $\mu\text{m}$  to about 120  $\mu\text{m}$ . [sic] The thickness of the film is preferably as thin as possible so as to allow for high manufacturing rates. However, as the film is made up of three layers, it is necessary for the thicknesses of the respective layers to remain great enough that they can be extruded. In addition, as the middle layer is preferably thicker than each of the outside layers, it is not possible in practice for it to drop below 30  $\mu\text{m}$ . In the example produced, the film had a thickness of 40  $\mu\text{m}$ , with a middle layer of 20  $\mu\text{m}$  and two outside layers of 10  $\mu\text{m}$ .

To allow the valve formed from the film that is the subject of this invention to close properly, this film has to have good flexibility. In the case of the LLDPE that forms the outside layers and forms part of the composition of the central layer, the flexibility is a function of the density  $d$ . This is why LLDPE was chosen, the density  $d$  of which can vary slightly within a range of between  $0.919 < d < 0.930 \text{ g/cm}^3$ . For PP, the flexibility is a function of the density and of the melt index MI. The density  $d$  can vary between  $0.895 < d < 0.905 \text{ g/cm}^3$ , while the melt index can vary between 0.75 and 0.85.

The Vicat temperature which is the softening temperature of the material, has to not differ too widely between the various layers in order to allow them to be coextruded. In the abovementioned example, the Vicat point  $T_v^\circ$  of the LLDPE must be greater than  $100^\circ\text{C}$ , while that of the PP must be less than  $160^\circ\text{C}$ . As

09875482 060601

a preference, these temperatures are between 110° and 150°C.

5 The proportion of slip agent, in this example Erucamide®, has to be less than 1300 ppm. Although this slip agent is needed only in the layer of the multilayer film adjacent to the face of this sheet that is intended to be situated on the inside of the valve passage, it is preferable for it to be incorporated into both outside layers, given that it is very difficult later to distinguish between these two outside layers and that there might therefore be a risk of the film being turned the wrong way up. By having both sides identical, this problem no longer exists.

15 As a preference, the film according to the invention, at least in its specific use for making the abovementioned valve, is not subjected to any corona oxidation treatment.

20 The single figure of the appended drawing depicts schematically and by way of example a plan view of a valve produced using a multilayer film that is the subject of the present invention.

25 This valve is intended to be inside a container, particularly a sealed sachet, not depicted, intended for packaging a liquid, particularly a drink. This figure shows two thicknesses 1a, 1b of this film which have been superposed. These two thicknesses of the film 1a, 1b are united by a weld line 2, creating between them a passage 3 forming the dispensing valve. A cut 4 allows the passage 3 to communicate with the outside, that is to say with the contents of the container. This passage 3 is normally closed, the two thicknesses of film 1a, 1b being contiguous. It is by introducing an element to part them that the valve opens and liquid can therefore flow between the inside of the container and the outside along the passage 3. The element used to open the passage 3 is itself formed by a pipe, particularly by a straw 5.

The end of this straw has a bulge 5a, as described in EP 98420015.4. The entry portion 3a of the

09075482 060601

valve passage 3 is narrowed and has a perimeter corresponding to that of the straw 5, so that this entry portion 3a fits around this straw 5 and opposes the passage of the bulged part 5a. In order to allow the straw 5 to be introduced through this narrowed entry portion 3a, the front end of the bulged part 5a of the straw 5 has a cross section that increases gradually, while the rear of this bulged part is connected by a bearing surface to the cylindrical part of the straw 5, which prevents it from coming back out through the entry portion 3a of the passage 3.

In order to obtain this fit of the entry portion 3a of the passage 3 around the straw, while however allowing the bulged part 5a to pass, the multilayer film 1a, 1b forming this valve has to have enough elasticity to close up again around the straw 5 once this bulged part 5a has passed. This is, in particular, one of the roles of the multilayer film that is the subject of the invention.

09875482 060601